



## [A] TIIVISTELMÄ - SAMMANDRAG

SUOMI - FINLAND

(FI)

*Jats 15.1.2005*  
PATENTTI- JA REKISTERIHALLITUS  
PATENT- OCH REGISTERSTYRELSEN

(11) (21) Patenttihakemus - Patentansökan 20035120

(51) Kv.lk.7 - Int.kl.7

C01B 31/02, B82B 3/00

(22) Hakemispäivä - Ansökningsdag 04.07.2003

(24) Alkupäivä - Löpdag 04.07.2003

(41) Tullut julkiseksi - Blivit offentlig 05.01.2005

(71) Hakija - Sökande

1 •Valtion teknillinen tutkimuskeskus, Helsinki, Vuorimiehentie 5, 02044 VTT, SUOMI - FINLAND, (FI)

(72) Keksijä - Uppfinnare

1 •Nasibulin, Albert, Servinkuja 2 B 18, 02150 Espoo, SUOMI - FINLAND, (FI)  
2 •Kauppinen, Esko, Jousimiehentie 10 L 93, 00740 Helsinki, SUOMI - FINLAND, (FI)  
3 •Brown, David, Vaasankatu 7 B 28, 00500 Helsinki, SUOMI - FINLAND, (FI)  
4 •Moisala, Anna, Haltijantontie 4-6 A 1, 02200 Espoo, SUOMI - FINLAND, (FI)

(74) Asiamies - Ombud: c/o VTT/Raimo Apunen  
PL 1000, 02044 VTT

(54) Keksinnön nimitys - Uppfinningens benämning

Menetelmä hiili-sipuli partikkelien valmistamiseksi  
Förfarande för framställning av kol-lök partiklar

(57) Tiivistelmä - Sammandrag

Uusi menetelmä onttojen sipuli-hiili partikkelien tuottamiseksi. Tarvitaan vain katalyyttiprekursori, hiili lähde, lämmön lähde ja virtauksen säätöjärjestelmä. Menetelmä käsittää seuraavat vaiheet: (a) reaktoriin viedään yksi tai useampi metallia sisältävä katalyyttipartikkeli, prekursori, yksi tai useampi hiili lähde, yksi tai useampi prekursori reagenssi. (mikäli tarvitaan katalyyttipartikkeli prekursorien tai hiili lähteiden kemialliseen hajottamiseen) ja yksi tai useampi kanto kaasu. (mikäli tarvitaan reaktoriolosuhteiden säätämiseksi); (b) hajotetaan yksi tai useampi katalyytti prekursori siirtymämetalleista tai niiden seoksista koostuvien katalyyttipartikkeleiden muodostamiseksi; (c) hajotetaan yksi tai useampi hiili lähde hiilen vapauttamiseksi; (d) pidetään materiaalit reaktorissa säädetyissä olosuhteissa säädety viipymäajan hiilikerroksen muodostamiseksi katalyyttipartikkeleille; (e) pidetään materiaalit reaktorissa säädetyissä olosuhteissa säädety viipymäajan katalyyttimetallin haihduttamiseksi partikkeliytimestä. Keksintö tuottaa onttoja sipuli-hiili partikkeleita, jotka muodostuvat yhdestä tai useammasta samankeskisestä hiilikerroksesta.

Nytt förfarande för producering av håliga lök-kol partiklar. Det behövs bara en katalytprecursor, en kolkälla, en värmkälla och en strömningskontrollsystem. Förfarandet innehåller följande steg: (a) införing till reaktorn en eller flera metal innehållande katalytpartikkel precursorer, en eller flera kolkällor, en eller flera precursor reagenser (vid behov för kemiskt sönderdelning av katalytpartikkel precursorer eller kolkällor) och en eller flera bärgaser (vid behov för kontrollering av omständigheterna i reaktorn); (b) sönderdelning av en eller flera katalytprecursorer för forming av katalytpartiklar bestående av övergångsmetaller eller deras blandningar; (c) sönderdelning av en eller flera kolkällor för frigöring av kol; (d) hållning av materialen i reaktorn i kontrollerade omständigheterna en kontrollerad tidsperiod för bildning av ett kolskikt på katalytpartiklar; (e) hållning av materialen i reaktorn i kontrollerade omständigheterna en kontrollerad tidsperiod för förflyktning av katalytmaterialet från partikelkämnan. Uppfinningen producerar håliga lök-kol partiklar bestående av en eller flera koncentrisk kolskikt.

# CARBON ONION PARTICLE SYNTHESIS

## BACKGROUND OF THE INVENTION

### 5           1. Field of the Invention

The present invention relates to a new method for gas phase synthesis of hollow carbon onion particles (COPs). The invention can be used for continuous or batch production of hollow COPs.

### 10           2. Description of related Art

Carbon onion particles, or simply nano-onions, are quasi-spherical carbon nanoparticles consisting of concentric graphitic shells. Nano-onions have been observed to either encapsulate metals or to consist of only carbon layers. The latter COPs may or may not contain an internal void. COPs with a void are termed hollow  
15   COPs. Voids may be complete or partial.

Various methods such as arc-discharge (Ruoff et al., "Single-crystal metals encapsulated in carbon nanoparticles" *Science* 1993; 259: 346), high-energy electron irradiation (Ugarte, "Curling and closure of graphitic networks under electron-beam irradiation" *Nature* 1992; 359: 707), thermal treatment of carbonaceous materials  
20   (Heer and Ugarte, "Carbon Onions Produced by Heat Treatment of Carbon Soot and Their Relation to the 217.5 nm Interstellar Absorption Feature" *Chem. Phys. Lett.* 1993; 207: 480), high-dose carbon ion implantation into metals (Cabioch et al., "Carbon onions formation by high-dose carbon ion implantation into copper and silver" *Surf. Coat. Tech.* 2000; 128-129: 43) and plasma-enhanced chemical vapour  
25   deposition (Chen et al., "New method of carbon onion growth by radio-frequency plasma-enhanced chemical vapor deposition" *Chem. Phys. Lett.* 2001; 336: 201) have been successfully utilized in the production of COPs. The formation of spherical hollow COPs and nickel-encapsulating COPs by an electric arc discharge method was reported in (Saito Y. "Nanoparticles and filled nanocapsules" *Carbon*  
30   1995; 33(7): 979). It was conjectured that hollow COPs could initially consist of Ni (or carbide) particles covered with graphitic layers where nickel atoms subsequently evaporated through defects in the outer graphitic carbon on the hot surface of the cathode. However, all of the described methods are fairly complicated and require high energy input. Moreover, nano-onions have mainly been produced as an  
35   unwanted by-product making the separation of carbon nano-onions from other carbon containing products an unavoidable process step.

The method described in this patent is a completely new approach to the production of hollow carbon nano-onions. It requires only a catalyst particle source (either through physical or chemical precursors), a carbon source, an energy source, and a flow control system. Here the term "physical precursor" means a source of particle precursor material that is vaporized by the addition of energy such as a resistively heated hot wire or arch discharge. The proposed method allows continuous production of hollow COPs and avoids certain intermediate stages such as catalyst preparation (as in chemical vapour deposition methods). In this method it is relatively easy to control the experimental conditions (such as temperature, residence time, and component composition) as compared to physical methods, and the experimental conditions inside the reactor can be readily determined by, for example, Computational Fluid Dynamics (CFD) calculations. Additionally, the method requires relatively low energy input with the correct choice of precursor chemicals or aerosol source thus making it industrially attractive.

COPs are expected to have properties suitable for many different applications most of which are similar to those of carbon nanotubes including magnetic storage media (especially for metal-encapsulating nano-onions), composite materials, and wear-resistant materials. Graphitic layers around particles protect encapsulated metal from the contamination from the surrounding atmosphere (nano shields). Such particles could, for instance, be used for storage of highly reactive metal containing particles. In particular, hollow COPs can also be used as effective thermoinsulator. Additional applications include dry lubricants, nano-tips in both Atomic Force Microscopy (AFM) and tunnelling microscopy and hydrogen storage media. The lack of suitable amounts of carbon nano-onions has previously restricted the development of their applications.

### SUMMARY OF THE INVENTION

The current invention provides a method for the continuous or batch synthesis of hollow carbon nano-onion particles in the presence of catalyst particles produced in a flow or batch reactor. This method comprises the steps of:

(a) introducing one or more metal containing catalyst particles or physical or chemical precursors thereof, one or more carbon sources, one or more precursor reagents (when needed for chemical decomposition of catalyst particle precursors or carbon sources) and one or more carrier gases (when needed for control of reactor conditions) into a reactor;

(b) when catalyst particle chemical precursors are present, decomposing one or more catalyst precursors to form metal catalyst particles consisting of transition metals or mixtures thereof;

(c) decomposing one or more carbon sources to release carbon;

(d) maintaining the materials in the reactor at controlled conditions and for a controlled residence time in order to form facilitate carbon formation on the formed catalyst particles;

5 (e) maintaining the materials in the reactor at controlled conditions and for a controlled residence time to allow catalyst metal to evaporate from the particle core.

The present invention can be realized in two basic configurations: for continuous COP production and for batch production of hollow COPs. The use of the flow reactor allows, however, continuous production of hollow COPs.

10 The present invention provides a composition of matter comprising hollow carbon onion-particles consisting of one or more concentric carbon layers surrounding a hollow core.

### **BRIEF DESCRIPTION OF DRAWINGS**

15 **Fig. 1** shows thermodynamic calculations of free Gibbs' energy of decompositions of example carbon sources at different temperatures.

**Fig. 2** shows a block diagram of an arrangement for the method for hollow COP production.

20 **Fig. 3** shows a preferred embodiment of the invention for COP production with a catalyst particle source via physical vapor nucleation from a decomposing gaseous precursor (a) and via physical nucleation from a hot wire (b) and from an arc discharge (c).

**Fig. 4** shows CFD calculations: velocity vectors and gas temperature contours for the given preferred embodiment of the invention operating with the  $\text{Cu}(\text{acac})_2$ - $\text{CO-N}_2$  system at  $t_{\text{furn}} = 1216^\circ\text{C}$  (inner flow rate of carbon monoxide  $Q(\text{CO}) = 330 \text{ cm}^3/\text{min}$  and outer flow rate of nitrogen  $Q(\text{N}_2) = 330 \text{ cm}^3/\text{min}$ ).

**Fig. 5** shows CFD calculations of contours of CO mass fraction for the preferred embodiment for  $\text{Cu}(\text{acac})_2$ - $\text{CO-N}_2$  system at  $t_{\text{furn}} = 1216^\circ\text{C}$  (inner flow rate of carbon monoxide  $Q(\text{CO}) = 330 \text{ cm}^3/\text{min}$  and outer flow rate of nitrogen  $Q(\text{N}_2) = 330 \text{ cm}^3/\text{min}$ ).

**Fig. 6** shows thermodynamic data of CO disproportionation: dependencies of free energy change,  $\Delta G$ , and CO mole fraction in gaseous phase on temperature. Kinetic data: CO concentration after disproportionation on surface of high porosity nickel catalyst.

35 **Fig. 7(a)** shows a sample alternate embodiment of the invention for continuous COP production.

**Fig. 7(b)** shows a sample alternate embodiment of the invention for batch COP production.

Fig. 8 shows TEM images of product synthesized at 1216 °C by  $\text{Cu}(\text{acac})_2$  decomposition ( $Q(\text{CO}) = 420 \text{ cm}^3/\text{min}$ ). ED patterns of product and ring simulations performed for copper are included in figure.

## 5 DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a continuous and a batch method to synthesize hollow COPs from a carbon source and metal catalyst precursor under controlled conditions.

### 10 1. Carbon source

According to the present invention, as a carbon source, various carbon containing precursors can be used. Carbon sources include, but are not limited to, gaseous carbon compounds such as methane, ethane, propane, ethylene, acetylene as well as liquid volatile carbon sources as benzene, toluene, xylenes, trimethylbenzenes. Alternatively and preferably, carbon monoxide gas can be used as a carbon source.

Thermodynamic calculations for decompositions of different carbon sources are presented in Fig. 1. This figure is provided to illustrate the variety of possible desirable carbon sources and does not, in anyway, limit the sources for which the present method can be applied. Note that increasing the temperature in the system generally makes the potential carbon sources less stable, except the reactions connected with carbon monoxide: CO disproportionation and the reaction between CO and  $\text{H}_2$ . Those reactions will be discussed further as related to the description of the preferred embodiment.

For other carbon sources, increasing the number of atoms in saturated hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ) generally leads to an increase in the instability of the substances. The stability behavior of systems with saturated carbon bonds from  $\text{C}_2\text{H}_2$  via  $\text{C}_2\text{H}_4$  to  $\text{C}_2\text{H}_6$  is not so obvious, because of its complex temperature dependency. Some liquid carbon sources are also included in this figure. One can see a trend for aromatic compounds (benzene  $\text{C}_6\text{H}_6$ , toluene  $\text{C}_6\text{H}_5\text{-CH}_3$ , o-xylene  $\text{C}_6\text{H}_4\text{-(CH}_3)_2$ , 1,2,4-trimethylbenzene  $\text{C}_6\text{H}_3\text{-(CH}_3)_3$ ). The most stable is the benzene molecule, where increasing the amount of methyl groups in the compound makes compounds less stable. Nevertheless, all of the presented compounds and many other carbon containing molecules can be used as a carbon source in the present invention. It is worth noting that the decomposition of carbon sources can occur even without the presence of catalyst particles, but because the decomposition is a kinetically limited process, a reasonable decomposition rate at moderate temperatures and relatively, low residence times can be obtained in the presence of catalyst particles.

In addition, the catalyst particles serve to decompose the carbon source at the location where carbon is integrated into the COP.

## 2. Catalyst Precursors

5 As catalyst material, various transition metals, which catalyzed the process of carbon source decomposition/disproportionation can be used. The catalyst particle can consist of transition metals and combinations thereof. Generally preferred for hollow COP production are catalyst systems based on copper, gold and silver because these metals have relatively high equilibrium vapor pressure and low carbon  
10 solubility.

Said catalyst particles can be introduced into the reactor or produced in the reactor by physical or chemical means. Physical means include physical nucleation of particles from a metal vapor source such as a hot wire or arch discharge. Additionally, catalyst particles can be introduced via chemical nucleation methods.  
15 For example, in the present embodiment,  $\beta$ -diketonate complex (copper (II) acetylacetonate,  $\text{Cu}(\text{acac})_2$ ) is used for the formation of the catalyst particles. Advantages of these precursors include suitable equilibrium vapor pressures, convenient decomposition temperatures and low toxicity. Alternatively, metal-organic, organometallic or inorganic compounds such as metallocene, and carbonyl  
20 compounds can be used as catalyst precursors.

## 3. Experimental design

Fig. 2 shows a block diagram of an arrangement for the continuous and the batch method for COP production. The first step of the scheme is to mix and to  
25 energize a carbon source and a catalyst precursor in the gas. Then, the formation of metal particles followed by the catalyst precursor decomposition occurs in the reactor. In the reactor, the carbon source catalytically decomposes/disproportionates. In order to form hollow carbon onions the evaporation of the embedded metal through the encapsulating carbon layers is needed. It is worth noting that the process  
30 of metal vapor evaporation and carbon graphitization can occur simultaneously. Also, the amount of void space and metal can be controlled by varying the reactor conditions and residence times.

## 4. Detailed description of the preferred embodiment of the invention

### 35 Description:

Fig. 3a. shows the preferred embodiment of the invention for a production of hollow COPs via solid catalyst precursor powders ( $\text{Cu}(\text{acac})_2$ ). In said embodiment, a flow of a carrier gas (pure nitrogen or carbon monoxide) is supplied from a carrier

gas reservoir (1) to the saturator (3) containing a catalyst precursor. As the carrier gas passes through the heated precursor, it is saturated by the precursor vapor. The method can be used to supply the catalyst precursor such as the precursor-carrier gas mixture enters a laminator (4) before entering the reactor (5). A carbon source is typically introduced into the system from the side from another gas cylinder (2) and separated before the reactor entrance by thin stainless steel tube (6). Nevertheless, the carbon source can be introduced through the saturator if it does not react with the catalyst precursor. Then it is possible to use a single gas for the carrier and carbon source. However, using two inlets for carrier gases allows one to vary the residence time and heating rate inside the reactor and also the concentration of the catalyst precursor (in addition to the saturator temperature) and the concentration of the carbon source. Inside the laminator (4), two separate steady state laminar flows containing the catalyst precursor vapor and carbon source are established. The flows are mixed and subsequently heated to a reactor temperature. Fig. 3b shows the equivalent embodiments when the source of catalyst particles is a hot wire generator (7) or arc discharge (12).

The presence of the laminator in the preferred embodiment of the invention is favored so as to produce the laminar flows in the reactor, which significantly simplify the equations for CFD calculations so as to more accurately characterize the system. Nevertheless, the invention does not require a laminar flow. Turbulent or transitional flows are also possible.

In the preferred embodiment of the invention a saturator has been used. The temperature of the saturator determined by equilibrium vapor pressure of the precursor and can be varied from room temperature to about 500 °C. For copper acetylacetonate, the operating saturator temperatures in the preferred embodiment are about 100 °C. Nevertheless, the invention does not require a saturator, some other methods can be used to provide suitable amounts of precursor. Additionally, the precursor gas need not saturate the carrier gas. The gas also can be undersaturated or supersaturated.

### CFD calculations

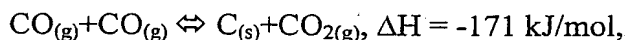
Computational Fluid Dynamics (CFD) calculations have been carried out for the present embodiment of the invention with a solid catalyst precursor (Fig.3a) to determine the temperature and velocity profiles and mixing conditions of the species in the reactor. The gas phase species transport and heat transfer were calculated with the StreamWise CFD program (Brown, D.P. Efficient Three-Dimensional CFD Model for Spray Combustion. NIST SBIR 97-1-58 Final Report, 1998) for experimental system of  $\text{Cu}(\text{acac})_2\text{--CO--N}_2$ . Grid resolution studies show a grid with

100 × 41 points was sufficient to resolve the phenomenon under consideration. The origin was chosen to be the outlet of the Cu(acac)<sub>2</sub> filter holder where the precursor was at known saturated conditions. The calculation was axisymmetric (since gravity is in the axial direction) which allowed the use of symmetry boundary conditions at the centerline. In addition to conservation of mass, momentum and energy, two gas phase species equations for CO and N<sub>2</sub> were solved. Buoyancy effects were included in the calculation. Inflow boundary conditions on mole fractions of the various species, inflow velocity, pressure, and temperature were the same as in the described experiments. Wall temperature boundary conditions were linearly interpolated from experimentally measured wall values. Inert wall boundary conditions were used for the gas phase species.

Fig.4 presents CFD calculations of velocity vectors and gas temperature contours for Cu(acac)<sub>2</sub>-CO-N<sub>2</sub> system at  $t_{furn} = 1216$  °C with the inner flow rate of  $Q(CO) = 330$  cm<sup>3</sup>/min and outer flow rate of  $Q(N_2) = 330$  cm<sup>3</sup>/min. Fig.5 shows the contours of CO mass fraction for this system at the same conditions. As one can see, there are small recirculation regions at the centreline at  $x = 0.1$  m due to buoyancy effects. The flow becomes fully developed once again beginning at  $x = 0.25$  m. The carbon monoxide and nitrogen gases were essentially completely mixed 0.1 m from the reactor inlet.

### Thermodynamic calculations

As a carbon source in the preferred embodiment of the invention, carbon monoxide is used. The reaction of CO disproportionation



which provides the carbon source, is exothermal and proceeds toward to the initial reagents at high temperatures. In Fig.6, the thermodynamic data of the disproportionation reaction, which include temperature dependencies of free energy  $\Delta G$  and equilibrium mole fraction of CO in gaseous phase, are presented. The reaction is seen to be inhibited at temperatures higher than about 900 °C (CO and CO<sub>2</sub> equilibrium composition is 97% and 3%, respectively). Moreover, kinetic investigations of carbon monoxide disproportionation on the surface of catalyst (Fig.6) showed that the appreciable reaction rates were achieved in the temperature interval from 520 to 800 °C with the maximum rate at a temperature of 670 °C. This means that, at high furnace temperatures ( $t_{furn} > 1000$  °C), the CO disproportionation reaction is likely to occur in the reactor before the high temperature zone, where the local temperature is lower than about 900 °C, and where the surface of catalyst particles are not yet passivated. It is worth noting that a similar temperature tendency is observed for the reaction between CO and hydrogen.



### 5. Description of sample alternate embodiment.

Fig.7(a) shows another embodiment, which could be used according to the present invention for a continuous production of the COPs. In this figure the system for the carbon source and/or catalyst precursor vapor introduction (8) is not specified. In case of solid and/or liquid catalyst precursor and/or carbon source, said saturator and/or bubbler can be used. For liquid substances, a bubbler, which consists of a vessel containing a liquid in which a tube with a carrier gas inserted, can be used. Room temperature is a suitable temperature for a necessary vapor pressure of some liquid catalyst precursors (as, for instance, for iron pentacarbonyl) and for some liquid carbon sources (as benzene, xylene, and toluene). Nevertheless, the vapor pressure of the liquid substance can be adjusted by heating or cooling the bubbler. Another possibility to decrease the vapor pressure of the liquid after the bubbler is to dilute the liquid with a suitable solvent. For instance, a mixture of benzene and cobalt carbonyl can be used to decrease the vapor pressure of  $\text{Co}(\text{CO})_4$ . Also some other methods for liquid catalyst precursor and/or carbon source introduction can be used such as droplet evaporation, liquid solution evaporation on the surface of heated substrate, etc. The reactor (5) can be, but is not necessarily, resistively heated (9), as in the case of the preferred embodiment of the invention, or some other energy sources can be applied to energize and decompose the precursor. For instance, it can be radio-frequency heating, microwave, acoustic, laser induction or some other energy source.

A sample alternate embodiment of the invention for the batch COP production is shown in Fig 7(b). After the introduction and mixing of a catalyst precursor and a carbon source through inlets (10) and (11), the volume is energized by means of energy input (9) whereupon COPs are formed inside the batch. Produced particles can be collected by means known in the art such as evacuation and filtering or thermophoretic deposition on a cold probe.

### EXAMPLE

In order to facilitate a more complete understanding of the invention, an example is provided below. These examples are for purposes of illustration only and not intended to limit the scope of the invention in any way.

The example illustrating the possibility of the synthesis of hollow COPs (Example 1) as a primary product was carried out in the same embodiment of the invention (Fig.3). The concentration of the precursor vapor after the saturator was determined by measurements of the mass difference of the removable precursor cartridge over a given period of time and varied by changing the flow rate through

the saturator and the saturator temperature. The temperatures of the saturator are maintained at 100 °C for  $\text{Cu}(\text{acac})_2$ .

#### Hollow carbon onion particles synthesis.

Energy source: resistively heated furnace.

Carbon source: CO.

Catalyst particle source: Chemical vapor nucleation.

Catalyst precursor:  $\text{Cu}(\text{acac})_2$ .

Operating furnace temperature: 1216 °C.

Operating flow rate: CO inner flow of  $Q(\text{CO}) = 420 \text{ cm}^3/\text{min}$ .

Operating catalyst precursor vapor pressure of 0.27 Pa.

The morphology and the size of the product are investigated with a field emission transmission electron microscope (TEM, Philips CM200 FEG). Electron diffraction (ED) patterns of the products were used for determination of the crystalline phase of metal particles. Fig.8 demonstrates the product formed at the operating conditions. The COPs consisted of several concentric carbon layers surrounding either a copper particle or a hollow core. Also copper particles completely covered by a graphitic shell were found among the product. The primary size of the copper particles ranged from about 5 to 30 nm according to TEM imaging, while carbon particles were from 2 to 50 nm in diameter and thoroughly agglomerated. The enclosed electron diffraction pattern of the product synthesized at this condition fit with the electron diffraction ring pattern simulations performed for pure copper, thus, the existence of copper carbides or oxides can be ruled out.

#### *Mechanism of hollow carbon onion particle growth in the current embodiment.*

Briefly and generally, four main processes taking place in the heated furnace leading to the formation of COPs can be distinguished. First, metal particle formation occurs as a result of the catalyst precursor decomposition and subsequently created supersaturated metal vapor in the system. The second process is the formation of the carbon atoms on the surface of catalyst particles. Thirdly is the formation of graphitic layers around particle after carbon crystallization. And finally the evaporation of the embedded metal through the defects in the carbon layers forming hollow COPs.

In particular, the mechanism of COP formation was studied using  $\text{Cu}(\text{acac})_2$  and CO as a catalyst precursor and carbon source, respectively. As mentioned previously, the CO disproportionation reaction occurs only at temperatures below 900 °C. Let us divide the reactor space into three parts: the first section is an initial

zone with the temperature less than 900 °C; the second section is a high temperature reactor zone; the third section is a cooling zone, where the temperature is dropping to ambient. CO disproportionation reaction occurs in the first, initial, zone. After the Cu(acac)<sub>2</sub> evaporation and heating of the vapor to a temperature above 300 °C, copper vapor formation occurs inside the furnace as a result of the Cu(acac)<sub>2</sub> decomposition reaction. The next stage is the formation of copper particles by vapor nucleation and condensation, and particle coagulation processes.

In the high temperature zone where released carbon forms graphitic layers around the particles, significant evaporation of copper through the carbon shells is expected to occur above the maximum temperature in the reactor. This happens because the equilibrium vapor pressure of copper (0.71 Pa) at the maximum furnace temperature of 1216 °C is higher than the catalyst precursor (0.27 Pa). It is worth noting that the temperature in this section is higher than the bulk copper  $T_{melt}=1083$  °C, which implies the copper particle exists in liquid form.

The CO disproportionation reaction can not occur in the cooling region, where favorable conditions for this reaction exist, because of the passivation of the catalytically active surface of copper particles.

## CLAIMS

What is claimed is:

1. A method for producing hollow carbon onion particles comprising the steps of:

- (a) introducing one or more catalyst particles or physical or chemical precursors thereof, one or more carbon sources, one or more precursor reagents (when needed for chemical decomposition of catalyst particle precursors or carbon sources) and one or more carrier gases (when needed for control of reactor conditions) into a reactor;
- (b) when catalyst particle chemical precursors are present and catalyst particles are produced via chemical vapor nucleation, decomposing one or more catalyst precursors to form metal catalyst particles consisting of transition metals or mixtures thereof;
- (c) decomposing one or more carbon sources to release carbon;
- (d) maintaining the materials in the reactor at controlled conditions and for a controlled residence time in order to facilitate carbon layer formation on the formed catalyst particles;

- (e) maintaining the materials in the reactor at controlled conditions and for a controlled residence time to allow catalyst metal to evaporate from the particle core.
2. A method according to claim (1) wherein the metal catalyst particle precursor is decomposed by the addition of energy from one or more energy sources.
3. A method according to claim (1) wherein the metal catalyst particle precursor is decomposed by the chemical reaction with one or more catalyst particle precursor reagents.
4. A method according to claim (1) wherein the carbon source is decomposed by the chemical reaction with one or more carbon source precursor reagents.
5. A method according to claim (4) wherein the catalyst particle precursor is a gas.
6. A method according to claim (4) wherein the catalyst particle precursor is a liquid.
7. A method according to claim (2) wherein the energy is thermal energy, microwave energy, acoustic energy, chemical energy, nuclear energy, electrical energy, laser energy.
8. A method according to claim (7) wherein the energy is provided by a resistively heated furnace.
9. A method according to claim (1) wherein the metal catalyst precursor is a metal containing compound.
10. A method according to claim (9) wherein the metal containing compound contains one or more metals.
11. A method according to claim (9) wherein the metal containing compound is a metalorganic, organometallic or inorganic compound.
12. A method according to claim (10) wherein the metalorganic compound is a metal acetylacetonate compound.
13. A method according to claim (12) wherein the metal acetylacetonate compound is  $\text{Cu}(\text{acac})_2$ .
14. A method according to claim (1) wherein the carbon source is a carbon containing compound.
15. A method according to claim (14) wherein the carbon containing compound is an organic or inorganic compound.
16. A method according to claim (15) wherein the organic compound is a hydrocarbon.

17. A method according to claim (16) wherein the hydrocarbon is liquid, gaseous or solid.
18. A method according to claim (17) wherein the gaseous hydrocarbon is  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ .
- 5 19. A method according to claim (17) wherein the liquid hydrocarbon is benzene  $\text{C}_6\text{H}_6$ , toluene  $\text{C}_6\text{H}_5\text{-CH}_3$ , o-xylene  $\text{C}_6\text{H}_4\text{-(CH}_3)_2$ , 1,2,4-trimethylbenzene  $\text{C}_6\text{H}_3\text{-(CH}_3)_3$ .
20. A method according to claim (17) wherein the solid hydrocarbon is  $\text{C}_{15}\text{H}_{32}$ ,  $\text{C}_{16}\text{H}_{34}$ ,  $\text{C}_{17}\text{H}_{36}$ ,  $\text{C}_{18}\text{H}_{38}$ .
- 10 21. A method according to claim (15) wherein the inorganic compound is carbon monoxide CO.
22. A method according to claim (1) wherein the precursor, carbon source, the precursor reagent and/or carrier gas are continuously introduced into the reactor which is maintained at steady state conditions and the products are continuously evacuated from the reactor to maintain a continuous production of product.
- 15 23. A method according to claim (1) wherein the precursor, carbon source, the precursor reagent and/or carrier gas are introduced into the reactor in which the conditions are changed with time and the products are later evacuated from the reactor to comprise a batch production of product.
- 20 24. A method according to claim (1) wherein the precursor reagent is needed for participation in the chemical reaction with catalyst particle precursor or carbon source in order to change the chemical rate of catalyst precursor or carbon source decomposition.
- 25 25. A method according to claim (24) wherein the precursor reagent is hydrogen.
26. A method according to claim (24) wherein the precursor reagent is water.
27. A method according to claim (1) wherein the metal catalyst particle is formed from a physical vapor source.
- 30 28. A method according to claim (27) wherein the vapor source is a resistively heated wire.
29. A method according to claim (27) wherein the vapor source is due to metal or alloy laser ablation.
30. A method according to claim (27) wherein the vapor source is due to metal or alloy arc discharge.
- 35 31. A method according to claim (27) wherein the vapor source is due to a conductively heated metal or alloy.

32. A method according to claim (27) wherein the vapor source is due to a radiatively heated metal or alloy.
33. A method according to claim (1) wherein the metal precursor is a liquid.
34. Particles prepared according to claims 1 to 33.
- 5 35. Particles according to claim 34, wherein the particles are formulated as a dispersion in a gas, a dispersion in a liquid, a dispersion in a solid, a powder, a tablet, a capsule or a colloidal suspension.
- 10 36. An insulating media, storage, wear resistant, lubricating, diagnostic, pharmaceutical, emitting, or surface altering composition comprising particles according to claim 34 or 35.

**ABSTRACT**

A new method for a production of hollow carbon onion particles is presented. It requires only a catalyst precursor, a carbon source, a heat source, and a flow control system. This method comprises the steps of: (a) introducing one or more metal containing catalyst particle precursors, one or more carbon sources, one or more precursor reagents (when needed for chemical decomposition of catalyst particle precursors or carbon sources) and one or more carrier gases (when needed for control of reactor conditions) into a reactor; (b) decomposing one or more catalyst precursors to form metal catalyst particles consisting of transition metals or mixtures thereof; (c) decomposing one or more carbon sources to release carbon; (d) maintaining the materials in the reactor at controlled conditions and for a controlled residence time in order to facilitate carbon layer formation on the formed catalyst particles; (e) maintaining the materials in the reactor at controlled conditions and for a controlled residence time to allow catalyst metal to evaporate from the particle core. The present invention provides a composition of matter comprising hollow carbon onion-particles consisting of one or more concentric carbon layers.

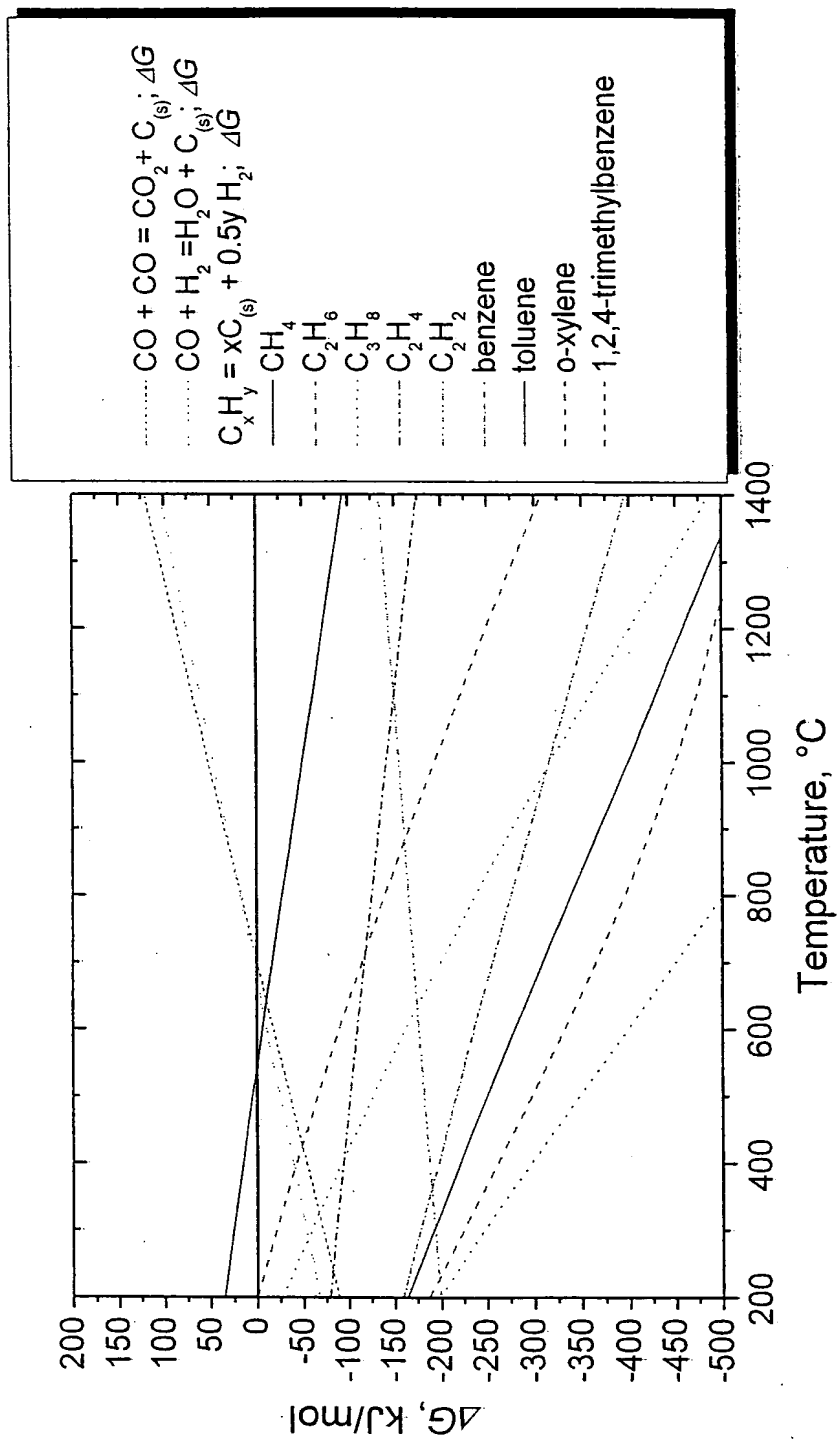


Fig. 1



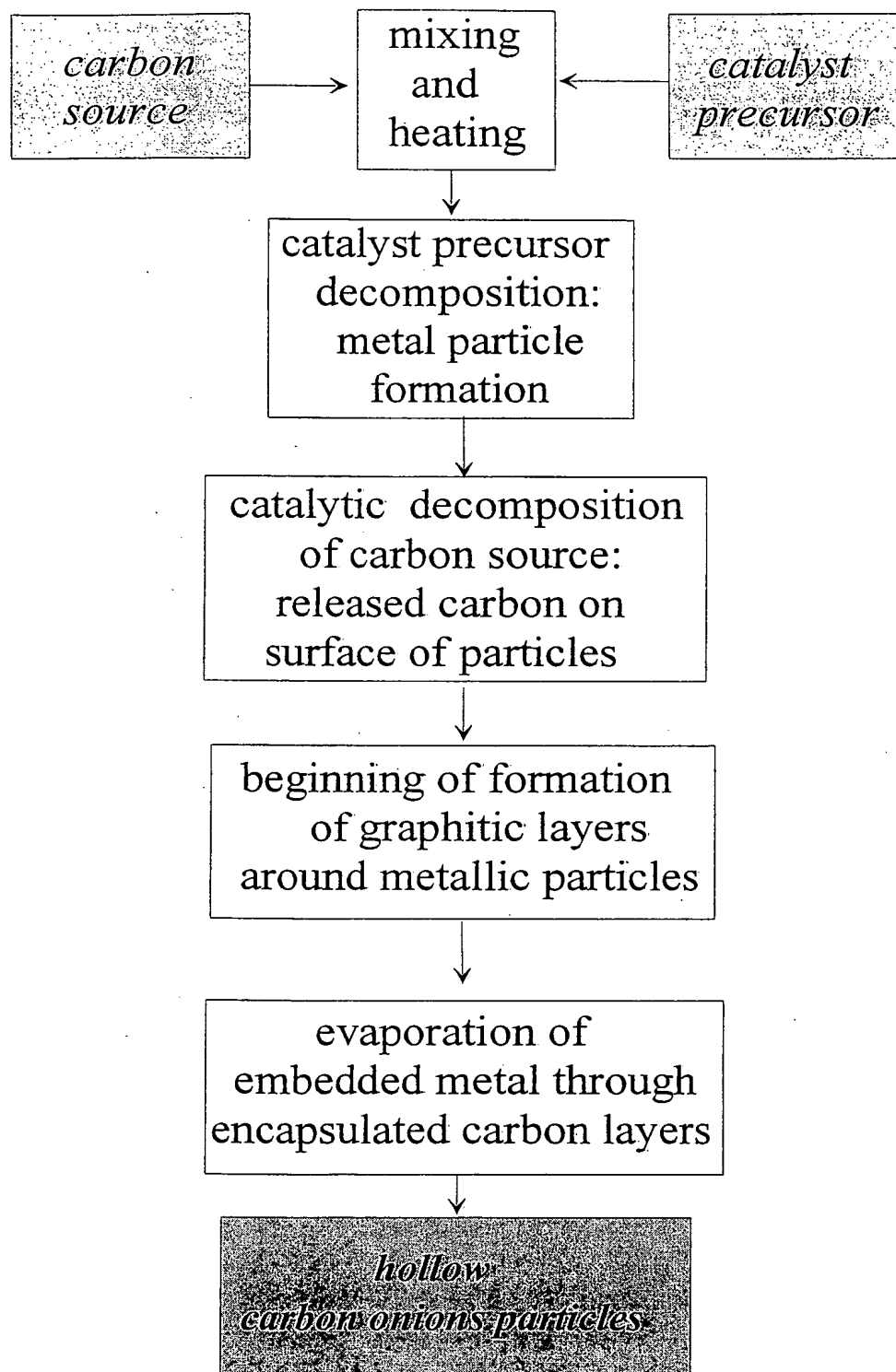
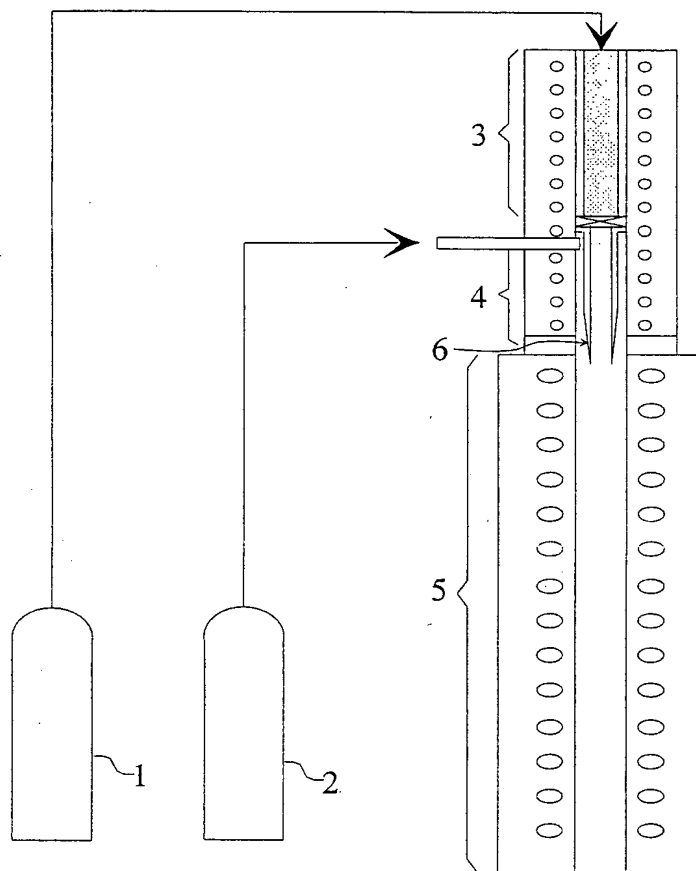


Fig. 2



**Fig. 3(a)**

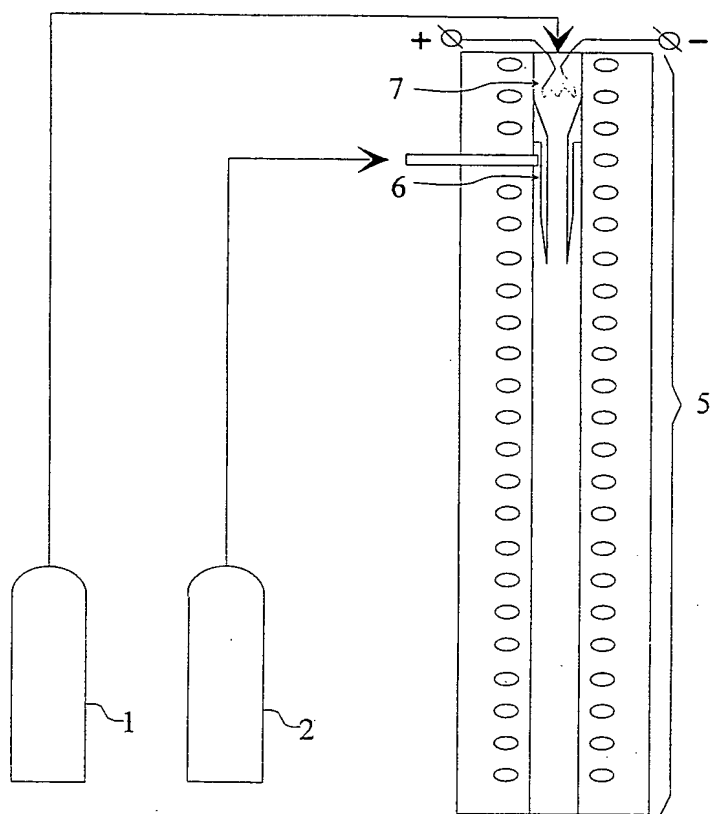
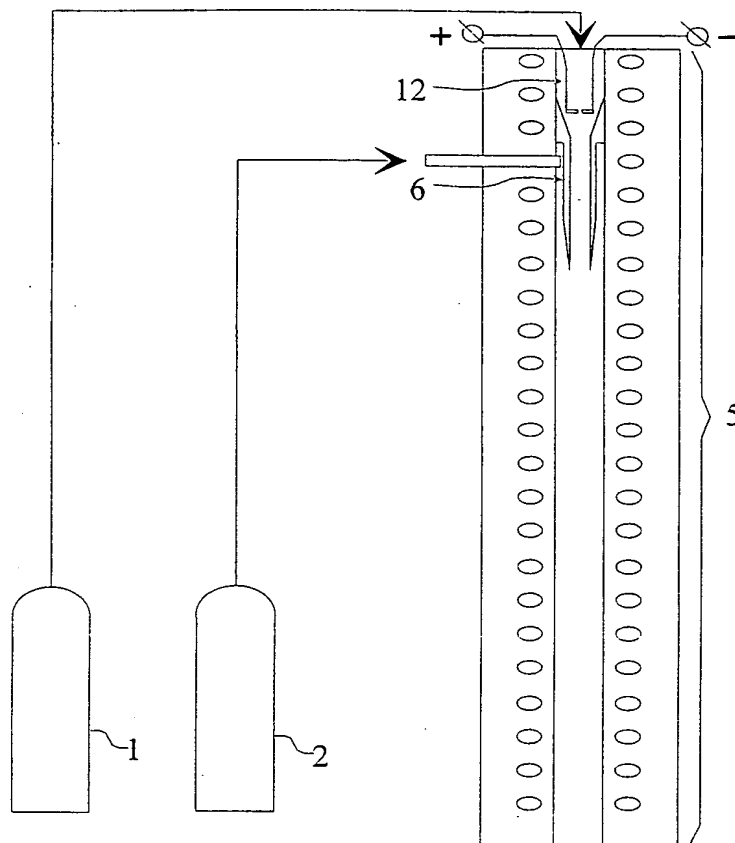


Fig. 3(b)



**Fig. 3(c)**

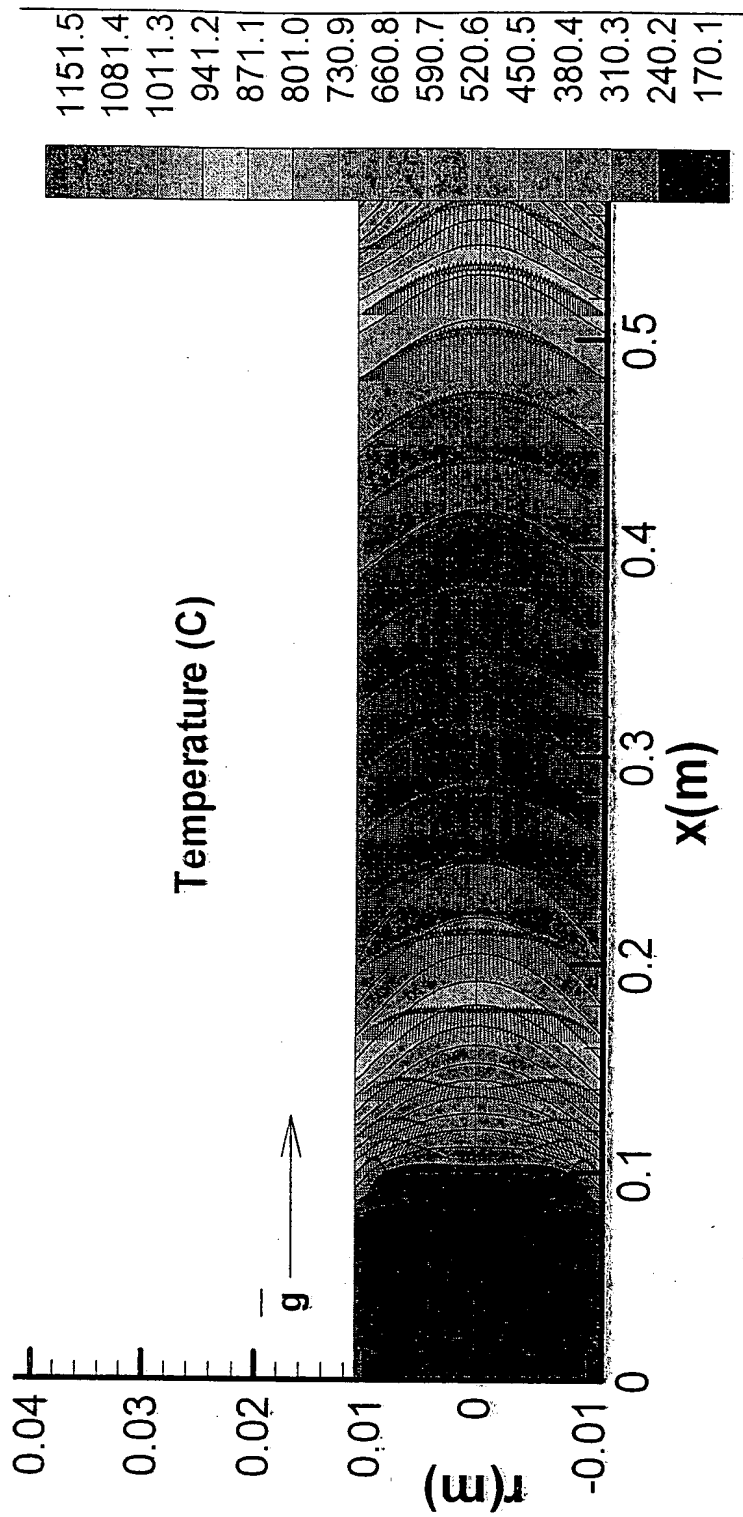


Fig. 4

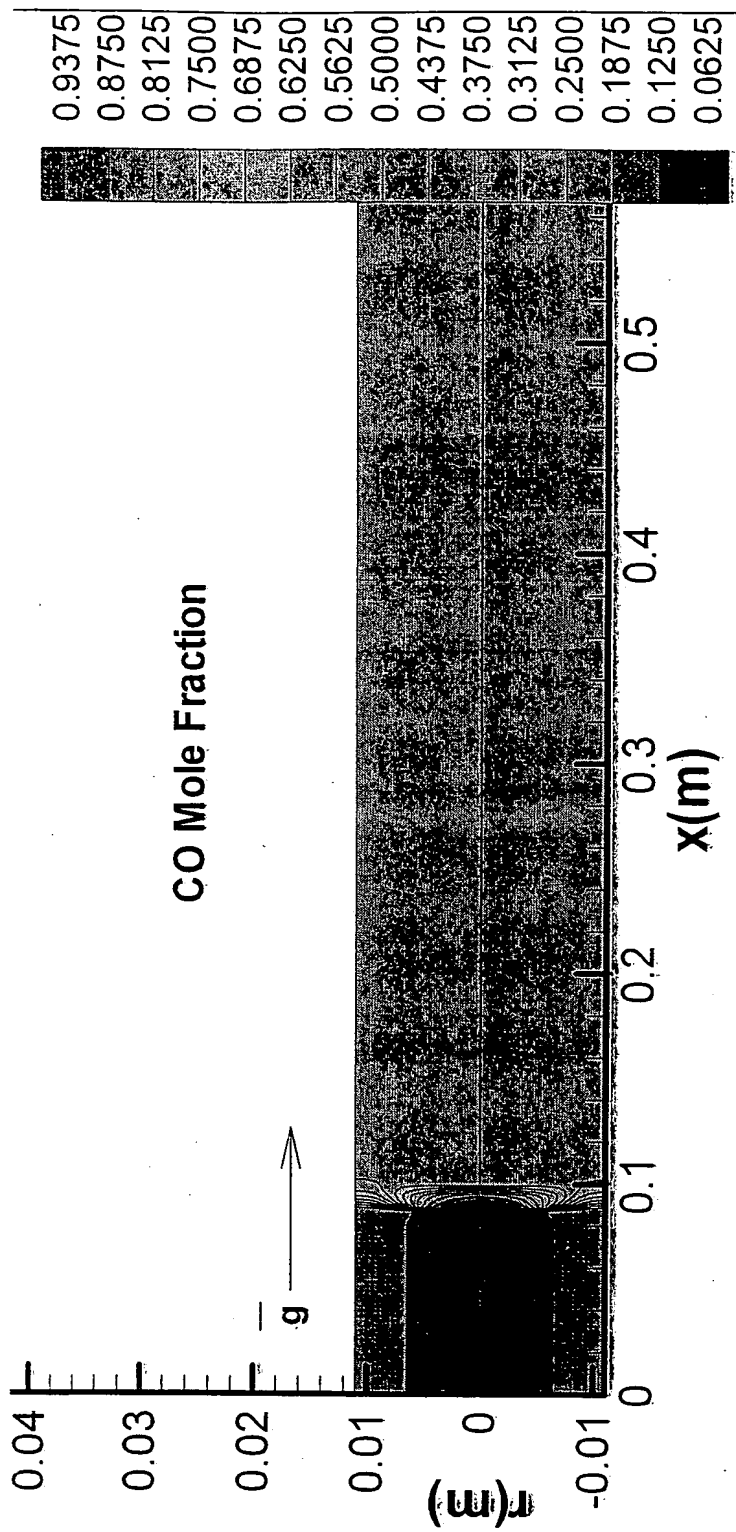


Fig. 5

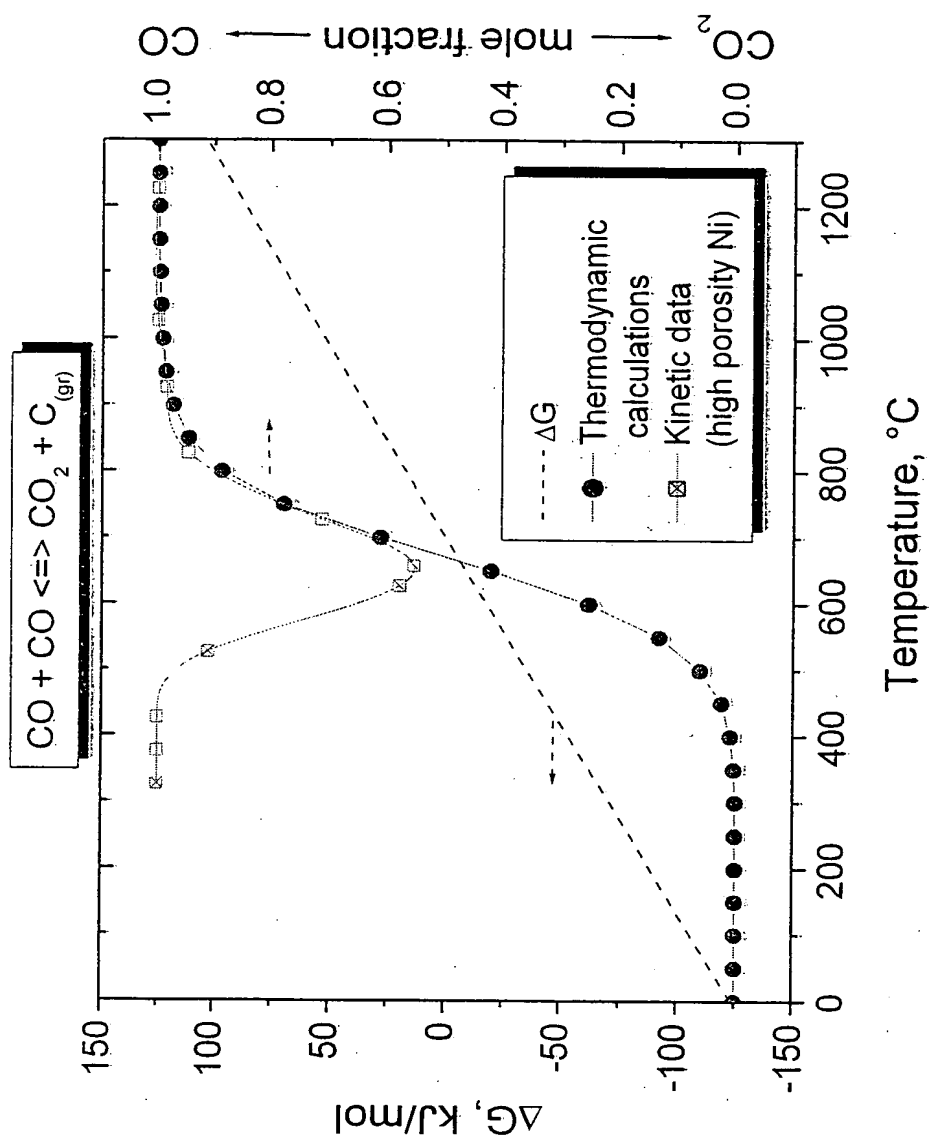
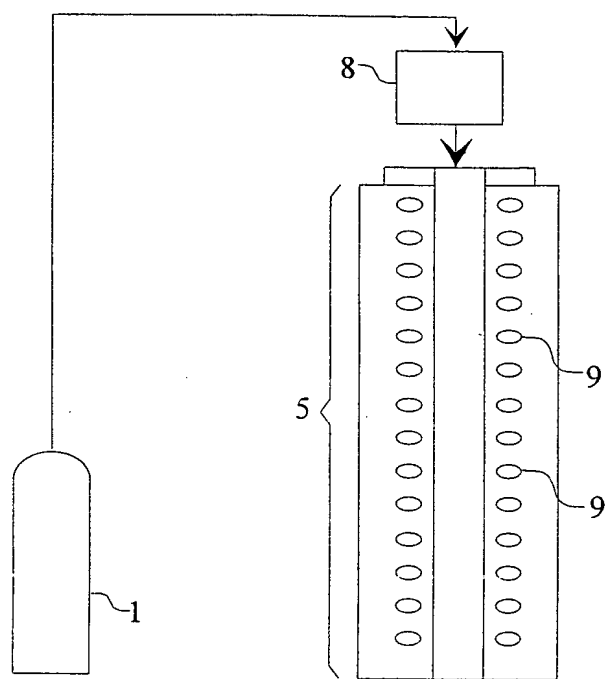


Fig. 6



**Fig. 7(a)**



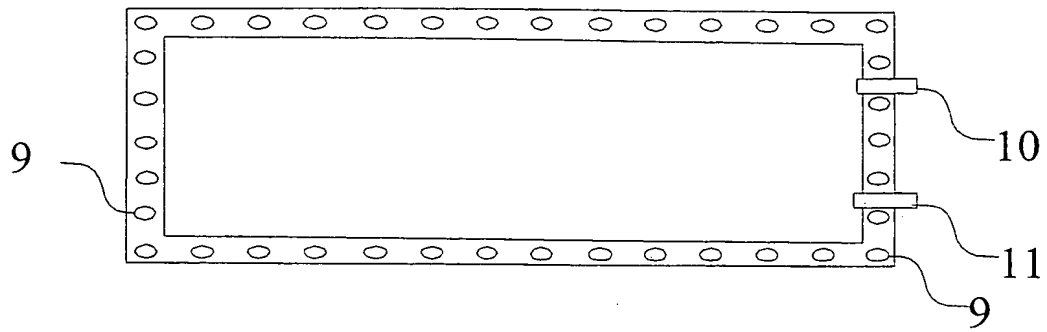
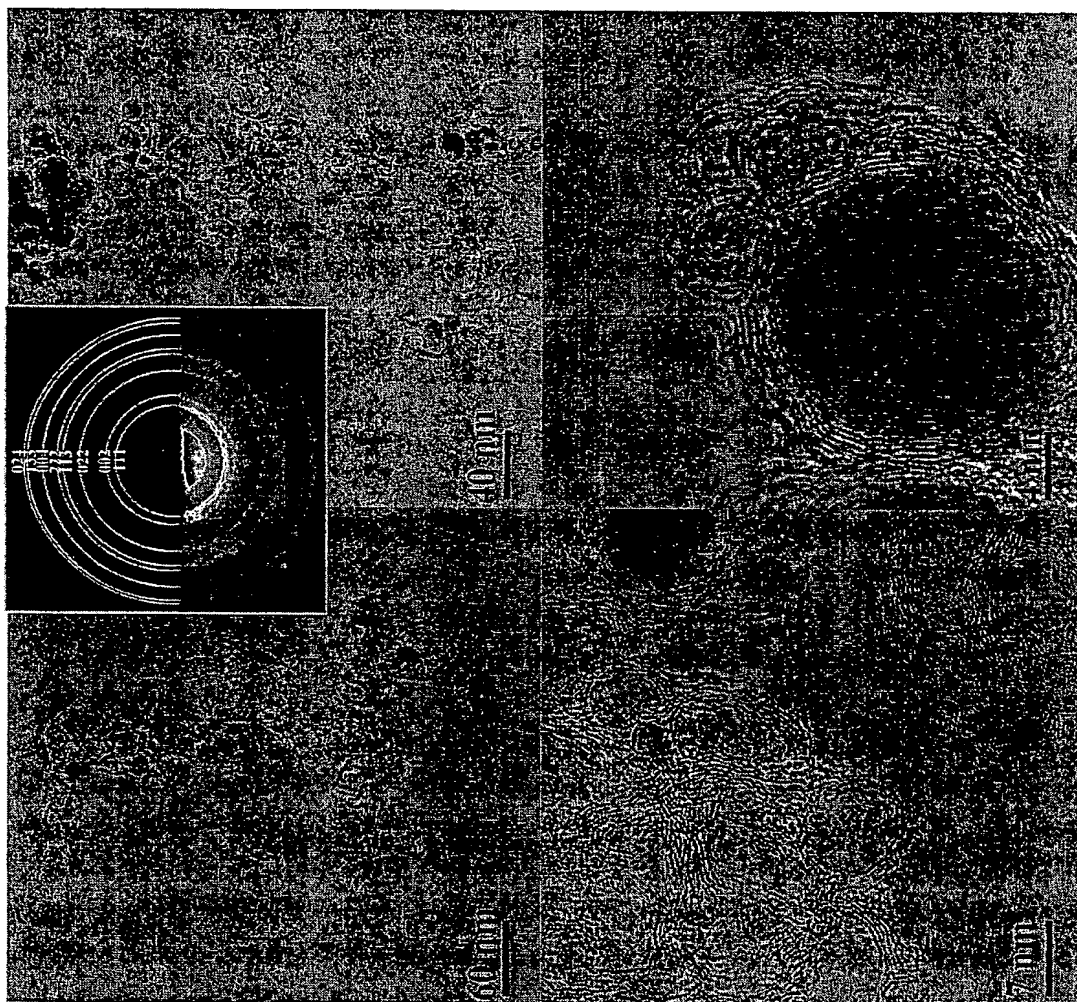


Fig. 7(b)



BEST AVAILABLE COPY

Fig. 8

**PATENTTI- JA REKISTERIHALLITUS**

Patentti- ja innovaatiolinja  
PL 1160  
00101 Helsinki

**TUTKIMUSRAPORTTI**

<b>PATENTTIHAKEMUS NRO</b>	<b>LUOKITUS, IPC7</b>
FI 20035120	C01B 31/02, B82B 3/00

**TUTKITUT PATENTTILUOKAT (luokitusjärjestelmät ja luokkatiedot)**

C01B, B82B

**TUTKIMUKSESSA KÄYTETYT TIETOKANNAT**

EPODOC, STN CAPLUS

**VIITEJULKAISUT**

<b>Kategoria*)</b>	<b>Julkaisun tunnistetiedot ja tiedot sen olennaisista kohdista</b>	<b>Koskee vaatimuksia</b>
X	Chem. Phys. Lett., 267(3,4), 1997, Elsevier, Sen & al. " Carbon nanotubes by the metallocene route"; s. 276-280	1-36

Jatkuu seuraavalla sivulla

☐

- \*) X Julkaisu, jonka perusteella keksintö ei ole uusi tai ei eroa olennaisesti ennestään tunnetusta tekniikasta.  
Y Julkaisu, jonka perusteella keksintö ei eroa olennaisesti ennestään tunnetusta tekniikasta, kun otetaan huomioon tämä ja yksi tai useampi samaan kategoriaan kuuluva julkaisu yhdessä.  
A Yleistä tekniikan tasoa edustava julkaisu.
- O Tullut julkiseksi esitelmän välityksellä, hyväksikäyttämällä tai muutoin muun kuin kirjoituksen avulla.  
P Julkaistu ennen hakemuksen tekemispäivää mutta ei ennen aikaisinta etuoikeuspäivää.  
T Julkaistu hakemuksen tekemispäivän tai etuoikeuspäivän jälkeen ja valaisee keksinnön periaatetta tai teoreettista taustaa.  
E Aikaisempi suomalainen tai Suomea koskeva patentti- tai hyödyllisyysmallihakemus, joka on tullut julkiseksi hakemuksen tekemispäivänä (etuoikeuspäivänä) tai sen jälkeen.  
D Julkaisu, joka on mainittu hakemuksessa.  
L Julkaisu, joka kyseenalaistaa etuoikeuden, osoittaa toisen julkaisun julkaisupäivämäärän tai johon viitataan jostakin muusta syystä.  
& Samaan patenttiperheeseen kuuluva julkaisu.

Lisätietoja liitteessä

☐

<b>Päiväys</b>	<b>Tutkijainsinööri</b>
10.02.2004	Liisa Helle